Lecture 7 - Introduction to sampling (MC & MD)

Last time:

Why is it for N, V, T

$$P(\underline{X}) \propto e^{-\beta \mathcal{H}(x)} = e^{-\beta \mathcal{H}(x)} / Z$$

$$A = -k_B T \ln Z$$

$$\mathcal{E} = -\frac{\partial \ln Z}{\partial \beta}$$

$$P = -\partial A / \partial V \quad \ldots$$

$$A = \mathcal{E} - T \frac{\partial A}{\partial T}$$

$$Z = \int dx\, e^{-\beta \mathcal{H}(x)}$$

$$\langle E \rangle = \langle \mathcal{H}(x) \rangle = \int dx\, \mathcal{H}(x)\, P(x)$$

$$= \int dx\, \mathcal{H}(x)\, \frac{e^{-\beta \mathcal{H}(x)}}{Z}$$

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z} \frac{\partial}{\partial \beta} \int dx\, e^{-\beta \mathcal{H}(x)}$$

$- \langle H(x) \rangle$

$$= \frac{1}{Z} \int dx\, (-\mathcal{H}(x))\, e^{-\beta \mathcal{H}(x)}$$

Ideal gas:

$$Z = Q \cdot N!\, h^{3N}$$

$$Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}N}$$

$$\varepsilon = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta}$$

$$\beta^{-3/2 N} \cdot \text{Stuff}$$

$$= -\frac{\partial}{\partial \beta} \ln\left[\beta^{-3/2 N}\right]$$

$$= \frac{3}{2} N \frac{\partial}{\partial \beta} \ln \beta = \frac{3}{2} N \beta^{-1} = \frac{3}{2} N k_B T$$

Heat capacity:

$$C = \frac{\partial E}{\partial T} \Leftarrow \text{extensive}$$

Extensive quantity $\propto$ system size

$\left\{ \begin{array}{l} \text{Energy is extensive} \\ T \text{ is not} \end{array} \right.$

$$c = C/N \sim \text{intensive}$$
$$= C/M$$

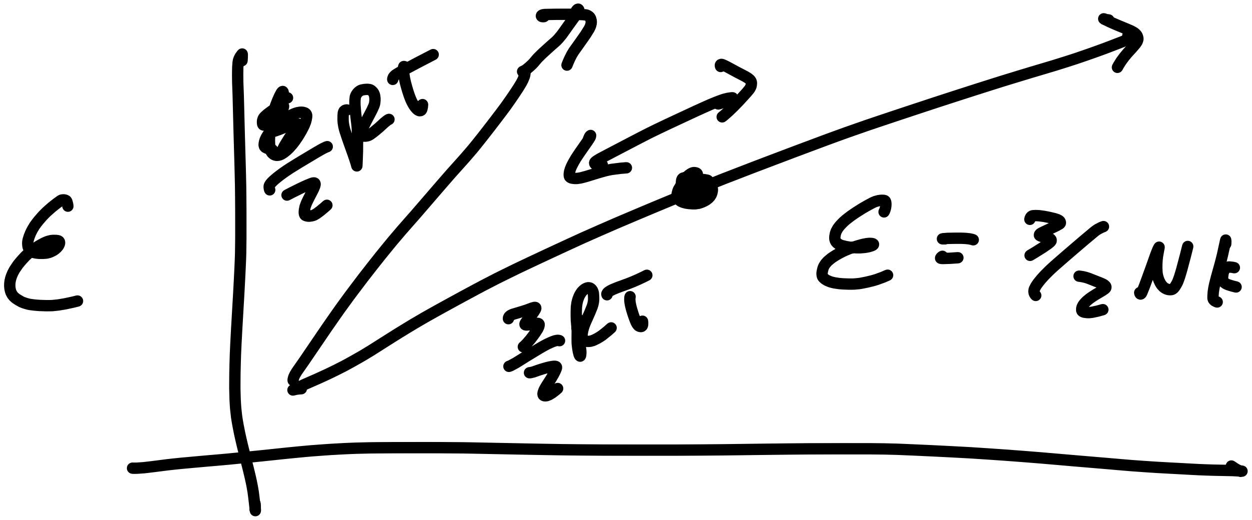
$\left[\begin{array}{l} \text{water:} \\ c \simeq \frac{1\ \text{Cal}}{g\,^\circ C} \end{array} \right.$

$$\simeq \frac{4.184\ J}{g\,^\circ C}$$

$$\rho \sim .997\ \frac{g}{mL}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V}$$

$$C_P = \left(\frac{\partial E}{\partial T} \right)_{N,P}$$



$$\mathcal{E} = \frac{3}{2} N k_B T$$

N, V, T const

$$C_V = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_{N,V} = \frac{3}{2} N k_B = \frac{3}{2} nR$$

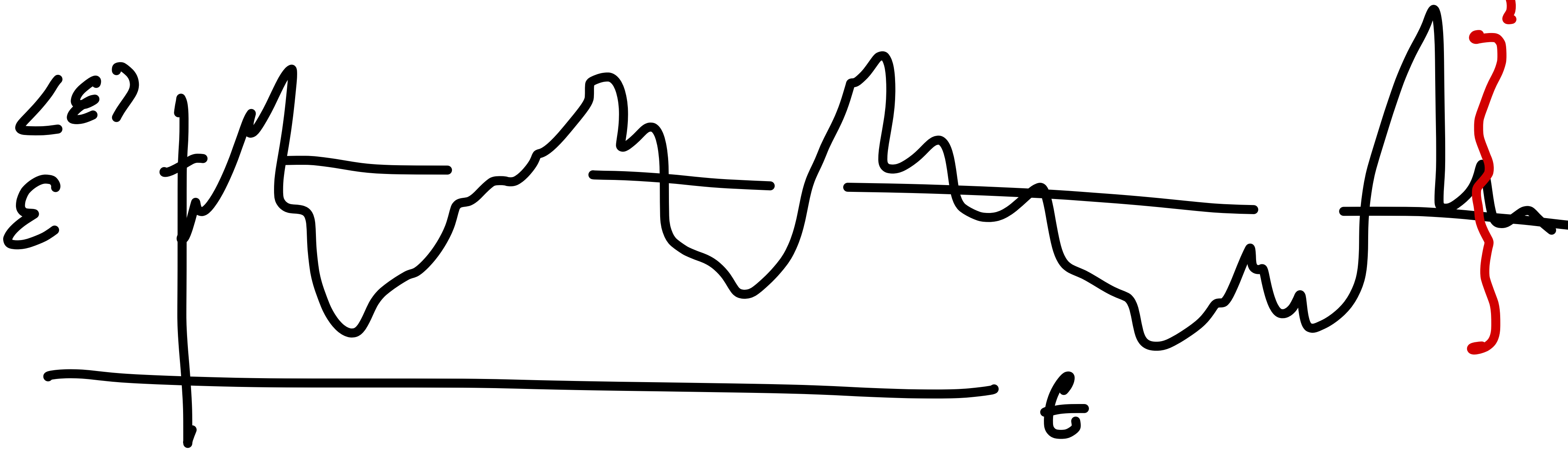
$$C_V/n = \frac{3}{2} R \approx \frac{3}{2} \cdot 8 \ \mathrm{J/K\,mol}$$

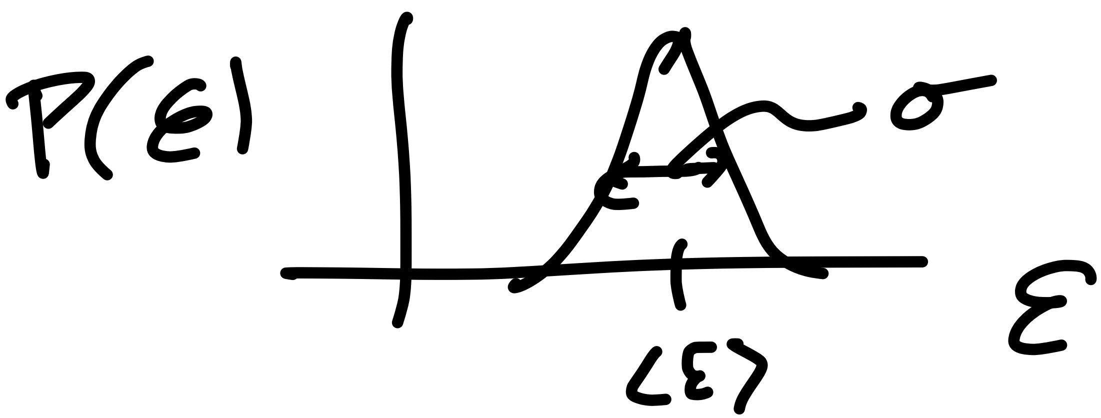
$$\approx 12 \ \mathrm{J/K\,mol}$$

$$C = \frac{\partial E}{\partial T} = \frac{1}{k_B T^2} \mathrm{Var}(E) = \frac{1}{k_B T^2} \sigma^2$$

std dev

@ const E fluctuates





$$\frac{\partial \langle E \rangle}{\partial T} \propto \mathrm{Var}(E)$$

Example of a fluctuation-dissipation theorem

Onsager Regression Hypothesis

$$\mathcal{E} = \langle E \rangle = \langle \mathcal{H}(\vec{x}) \rangle$$

$$C = \frac{\partial E}{\partial T} = \left(\frac{\partial E}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right)$$

$$\beta = \left(1/k_B T\right) \qquad \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$-\frac{1}{k_B T^2} \cdot \frac{\partial E}{\partial \beta} \leftarrow -\frac{\partial \ln Z}{\partial \beta}$$

$$= +\frac{1}{k_B T^2} \frac{\partial}{\partial \beta}\left[\frac{\partial \ln Z}{\partial \beta}\right] = +\frac{1}{k_B T^2} \frac{\partial}{\partial \beta}\left[\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right]$$

$$= \frac{1}{k_B T^2}\left[\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} + \frac{\partial Z}{\partial \beta}\left(-\frac{1}{Z^2}\frac{\partial Z}{\partial \beta}\right)\right]$$

$$= \frac{1}{k_B T^2}\left[\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} + \frac{\partial Z}{\partial \beta}\left(-\frac{1}{Z^2}\frac{\partial Z}{\partial \beta}\right)\right]$$

$$-\frac{1}{Z^2}\frac{\partial Z}{\partial \beta}\frac{\partial Z}{\partial \beta} = -\left[\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right]\left[\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right]$$

$$- \quad \langle \varepsilon \rangle \quad \langle \varepsilon \rangle$$

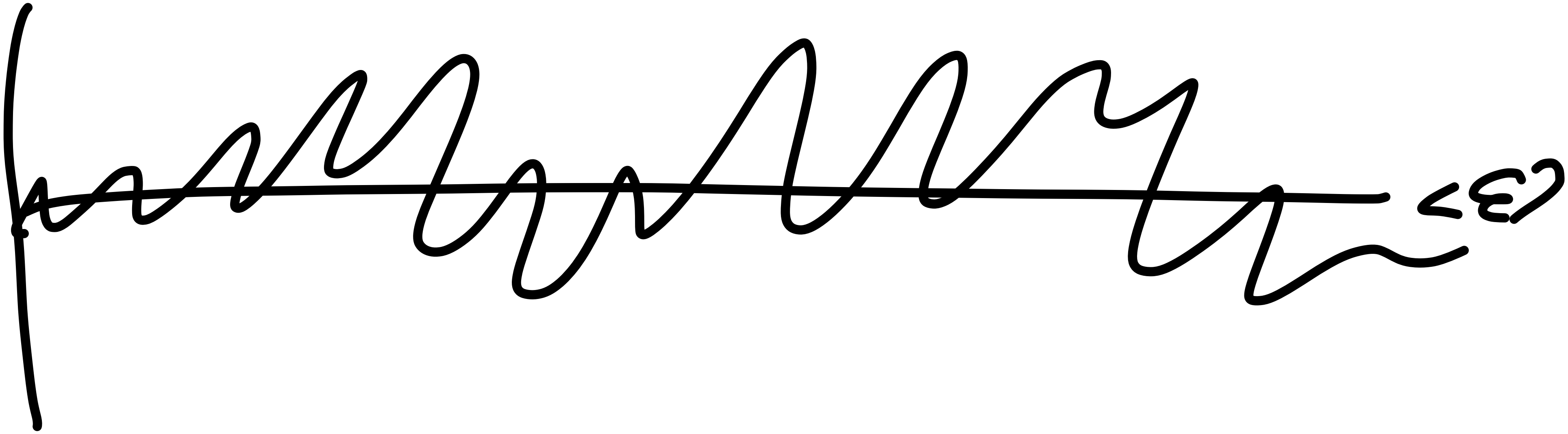
check

$$\langle \varepsilon^2 \rangle = \int dx\, \mathcal{H}(x)^2 e^{-\beta \mathcal{H}(x)} / Z$$

$$\frac{\partial \varepsilon}{\partial T} = \frac{1}{k_B T^2}\left[\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2\right]$$

Var(ε)

$\langle (\varepsilon - \langle \varepsilon \rangle)^2 \rangle$

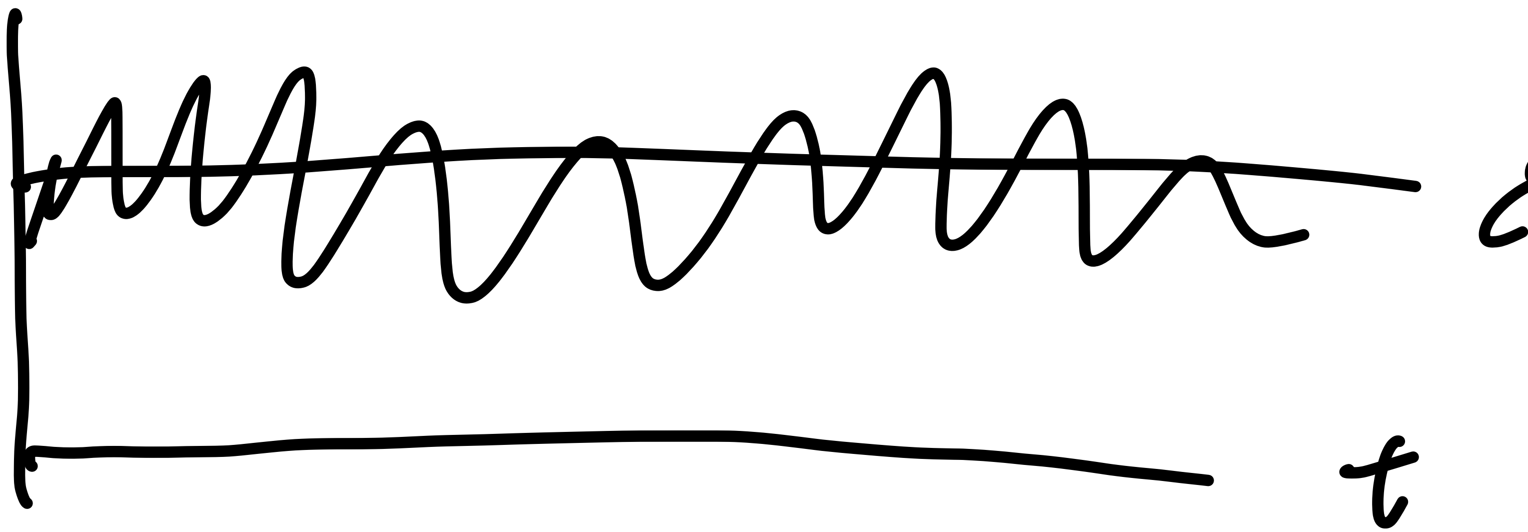


how big is σ_ε as compared to $\langle \varepsilon \rangle$

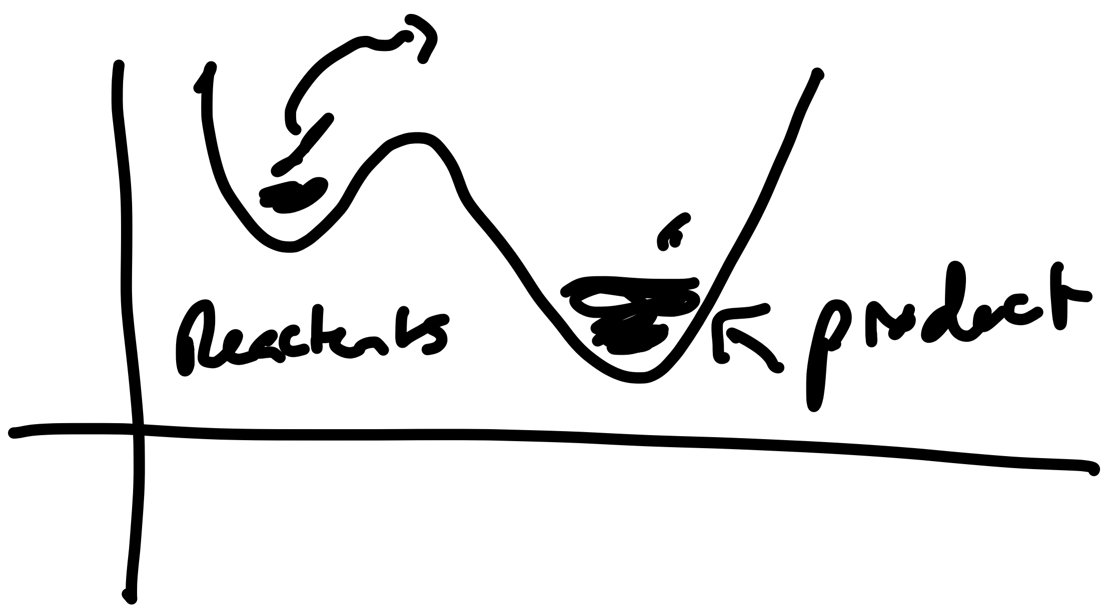
$$\sigma_\varepsilon / \varepsilon = \frac{\sqrt{\mathrm{Var}\,\varepsilon}}{\varepsilon} \propto \sqrt{C_V}/\varepsilon \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

C_V – extensive $\propto N$ – $\dfrac{[\varepsilon]}{[T]}$

ε – extensive $\propto N$

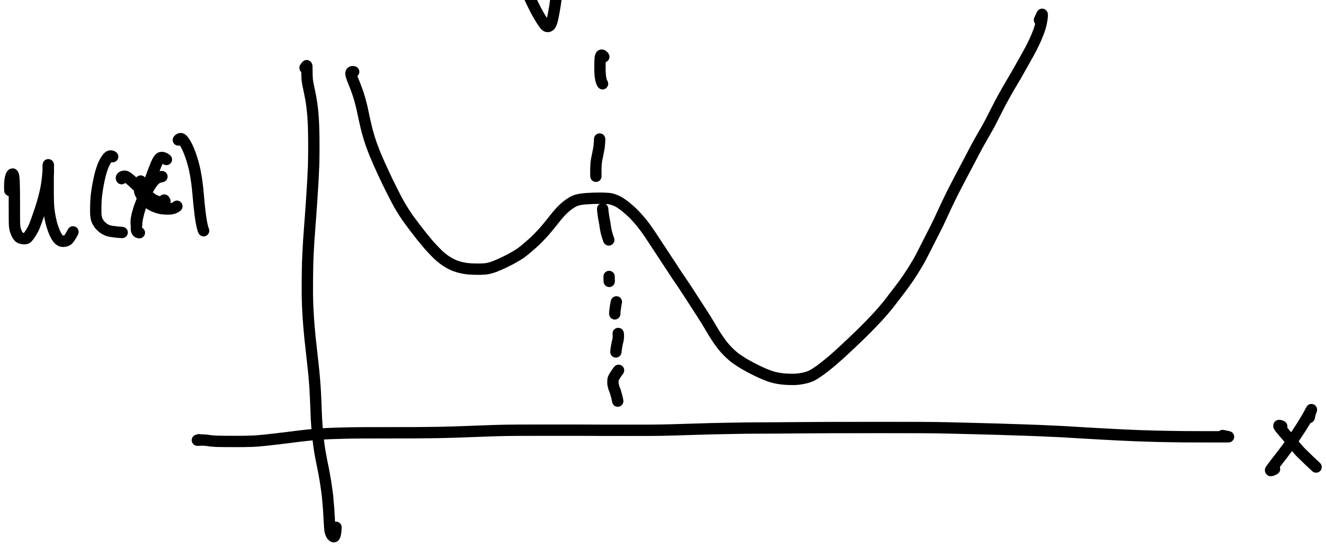


Fluctuations in E are what allow chemical reaction to happen



Want are average observables

$$\langle O \rangle = \int P(\vec{x})\, O(\vec{x})\, d\vec{x}$$



$$\langle O \rangle = \int d\vec{x} \int d\vec{p}\; O(\vec{x}, \cancel{\vec{p}})\, e^{-\beta \mathcal{H}(\vec{x}, \vec{p})} \Big/ Z$$

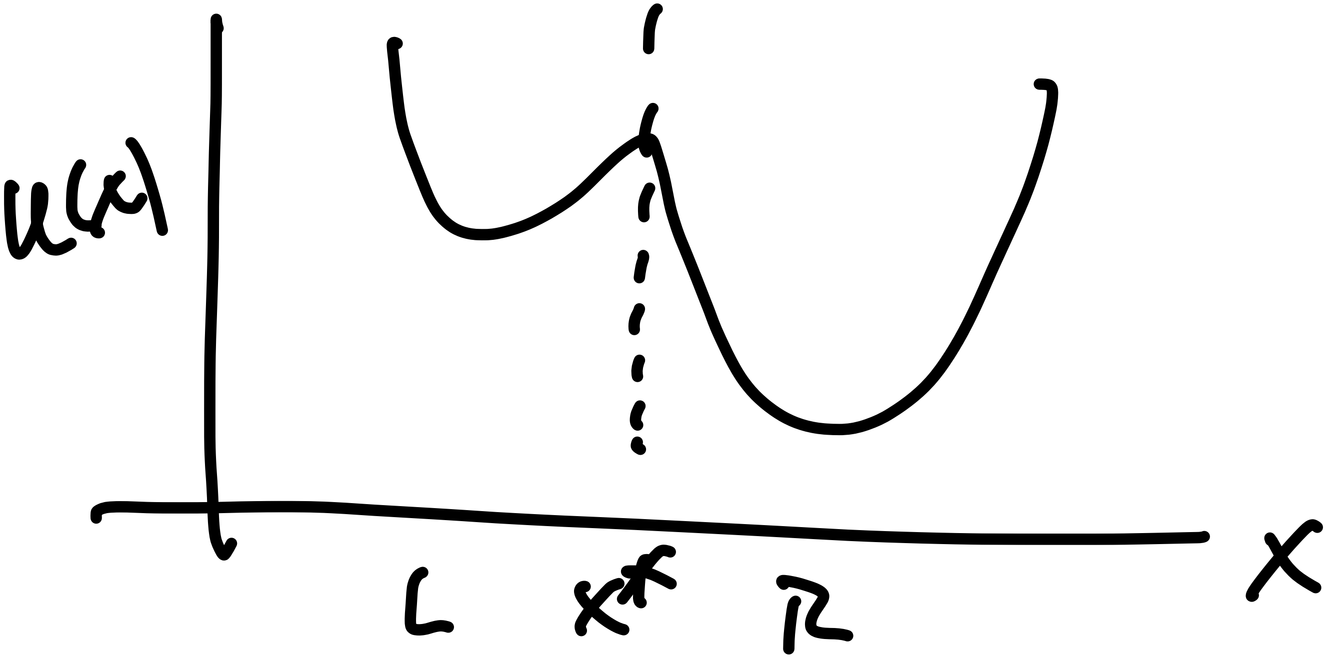
$$\mathcal{H}(\vec{x}, \vec{p}) = \sum_i \vec{p}_i^{\,2} / 2m_i + U(\vec{x})$$

$$\langle O \rangle = \frac{\cancel{\int d\vec{p}\, e^{-\beta \sum p_i^2/2m_i}} \int d\vec{x}\, O(x)\, e^{-\beta U(x)}}{\cancel{\int d\vec{p}\, e^{-\beta p_i^2/2m}} \int d\vec{x}\, e^{-\beta U(x)}}$$

if O depends only on position

$$= \int d\vec{x}\, O(x)\, e^{-\beta U(x)} \Big/ Z_{(\text{position})}$$

$$Z_{(\text{pos})} = \int d\vec{x}\, e^{-\beta U(x)}$$

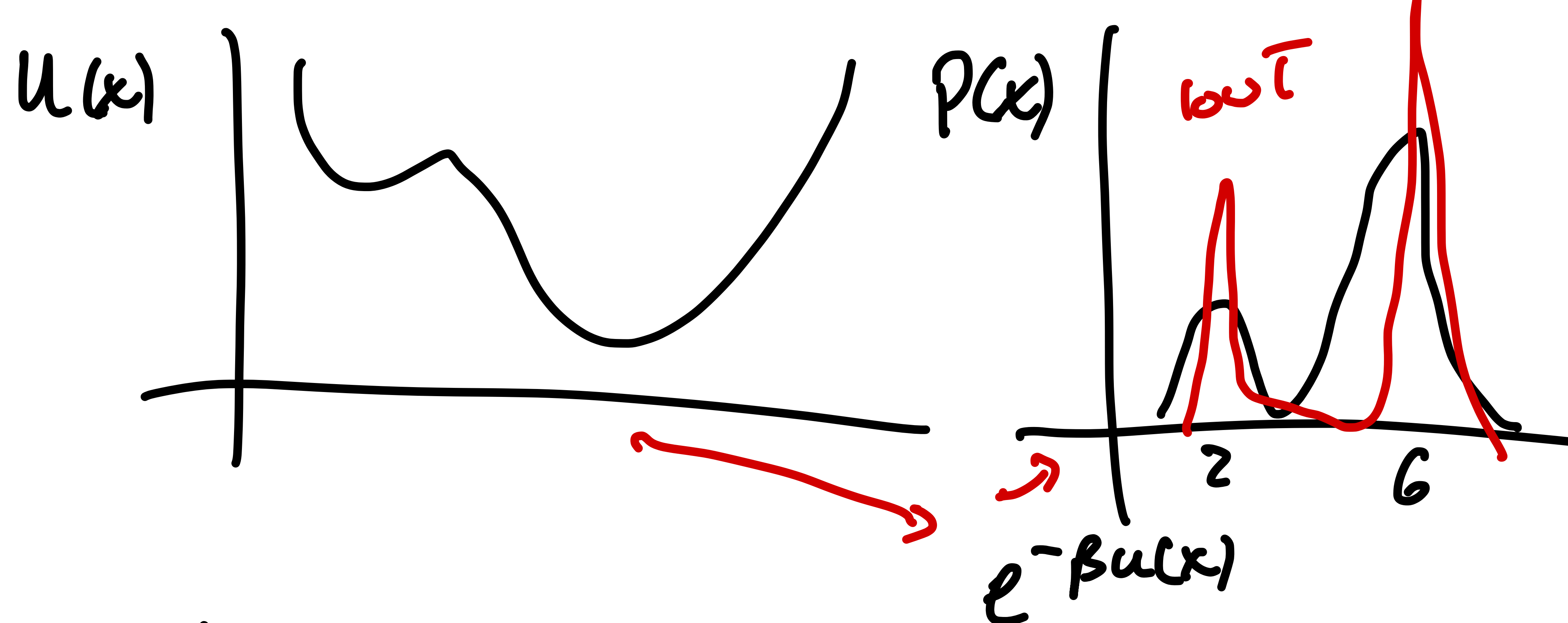


folded / unfolded
bound / unbound

eg $\langle \text{in state } L \rangle$ $\qquad \chi_L = \begin{cases} 1 & \text{if } x < x^* \\ 0 & \text{otherwise} \end{cases}$

$$\langle O \rangle = \int O(x)\, e^{-\beta U(x)}\, dx \Big/ \int dx\, e^{-\beta U(x)}$$

$$= \int O(x)\, P(x)\, dx$$



$$\approx \sum O_i P_i \quad @ \text{ low } T$$

$$\langle O \rangle = \int O(x)\, P(x)\, dx$$

$$\approx \sum_i \Delta x\, O(x_i) P(x_i)$$

Evaluation by quadrature

Usually know $U(\vec{x}) \rightarrow P(x)$

for each dimension

$\#$ points $= L/\Delta x$

in d:

$(L/\Delta x)^d$

$$\left(L/\Delta x\right)^d = e^{d \ln(L/\Delta x)}$$

exponentially large in d

$$d = 3N$$

Idea of sampling:

if we generate "samples"

x_t apper with prob $P(x_t)$

$$\langle O \rangle \approx \frac{1}{T}\sum_{t=1}^{T} O(x_t)$$

$x_1 \rightarrow x_2 \rightarrow x_3 \rightarrow \cdots \rightarrow x_\tau$

recipe for this

- Molecular dynamics

  Newton's Eqns (w/T)

- Monte Carlo sampling